

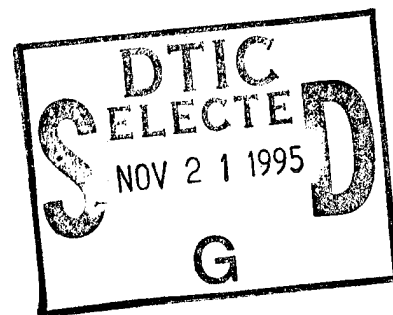
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Cooperative Motion of Side Groups in Amorphous Polymers: Dipolar Interactions

by

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COOPERATIVE MOTION OF SIDE GROUPS IN AMORPHOUS POLYMERS: DIPOLAR INTERACTIONS

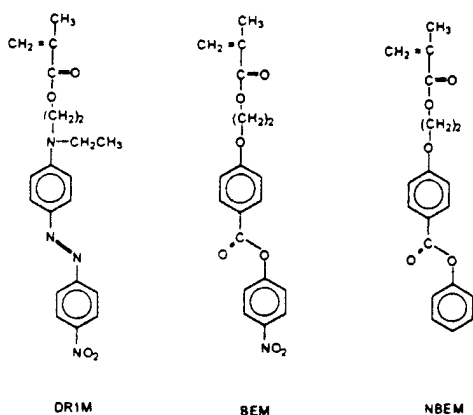
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INTRODUCTION

We have recently reported a cooperative motion in amorphous polymers containing polar azobenzene and ester rigid groups¹. When the azobenzene groups are photochemically oriented through isomerization induced by polarized light, the ester groups move in concert to produce a significant increase in the photoinduced birefringence (up to four times). The experiments were performed on films of copolymers of 4'-[(2-(methacryloyloxy)ethyl) ethylamino]-4-nitroazobenzene (DR1M) 4-nitrophenyl 4'-[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]oxy] benzoate (BEM) shown in Scheme 1.

Scheme 1



Such cooperative motion is well known in side-chain liquid crystalline polymers and is driven in that case by the thermodynamic tendency to align. Such a tendency does not exist in poly(DR1M-co-BEM), and the explanation for the cooperative motion may be either a dipolar interaction (both groups have dipole moments of about 7D) or a steric factor (minimizing the free volume necessary for motion) or a combination of both. To answer this question, copolymers of DR1M with a less polar analogue of BEM have been synthesized and their photochemical behavior investigated. The monomer (shown above) is 4-phenyl-4'-[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]oxy]benzoate (NBEM), with a dipole moment of only 0.95 D (calculated from molecular models).

EXPERIMENTAL

DR1M, BEM and NBEM were synthesized as previously described¹ and by a slightly modified method. The polymerization of DR1M, BEM and NBEM and their copolymerizations were carried out in dioxane or toluene at 60 °C initiated with AIBN. The polymers obtained were purified by reprecipitation twice from methanol.

The procedure for reversibly introducing birefringence on a polymer film using a polarized/circularly polarized laser beam has been previously described². Electronic spectra were recorded on a Shimadzu Spectrometer.

RESULTS AND DISCUSSION

Monomers and Copolymers. The reactivity ratios obtained for the DR1M/BEM pair and for the DR1M/NBEM pair are $r_{\text{DR1M}} = 1.03$, $r_{\text{BEM}} = 0.82$ and $r_{\text{DR1M}} = 0.83$, $r_{\text{NBEM}} = 1.13$ respectively. As is expected for methacrylates having similar structures, these ratios are similar and near unity, showing no strong preference for either monomer. All copolymers are amorphous as determined by DSC and polarized microscopy. Since BEM and NBEM are quite similar in structure (bonding, shape and size) but have different dipole moments, a comparison of these two systems should be expected to elucidate the polarity effect on the photoinduced orientation.

Absorption Spectra. Similar to that found in poly(DR1M-co-BEM) series¹ the electronic spectra of poly(DR1M-co-NBEM) films also show a shift of the visible absorption maximum. The magnitude of the shift is a function of the azo structural units content in the copolymer, as shown in Figure 1. At the same DR1M content, the λ_{max} for BEM copolymer films are larger than for NBEM copolymer films. This is because BEM associates with DR1M as a polar "solvent" inducing a red shift of the azo chromophore absorbance, similar to results in solution reported by Whitten and coworkers³. The red shift for very low azo contents is comparable to that obtained for copolymers of DR1M with methyl methacrylate (MMA)⁴. Thus, for an intramolecular interaction point of view, the effects of "nonpolar" NBEM and MMA of DR1M are similar. This obviously also confirms that the interaction between BEM and DR1M is stronger than that between NBEM and DR1M groups.

Photoinduced birefringence. The saturated levels of induced birefringence in poly(DR1M-co-BEM) and poly(DR1M-co-NBEM) films are plotted as a function of the DR1M structural unit weight fraction in Figure 2. A linear increase in the photoinduced birefringence with the azo content is found for the NBEM copolymers. Since the birefringence is supposed to arise from the orientation of the azo groups, one would expect a linear dependence of the birefringence on the weight fraction of the azo groups. This is

what happens in blends of a homopolymer containing azo groups in each structural unit with an "inert" homopolymer (poly(MMA))⁴. The linear dependence on azo weight fraction clearly indicates that if there is any cooperative motion between the DR1M and NBEM groups, it certainly contributes a negligible amount to the overall birefringence of the copolymer.

The behavior of poly(DR1M-co-BEM) is quite different, as previously reported¹. The birefringence of poly(DR1M-co-BEM) increases fast with the azo concentration up to about 40 %, then it becomes almost constant at about the same value as poly(DR1M). The increase of birefringence in comparison with poly(DR1M-co-NBEM) is directly related to the presence of the BEM groups¹.

The obvious difference between the two copolymer series presented here is the polarity of the ester group. When the ester group is almost nonpolar, all the birefringence in the copolymer films comes from the orientation of the azo groups. When the ester group has a polarity similar to the azo group, the two types of groups move together driven by the photoselection process which only the azo groups undergo. If the steric factor would be important in this concerted motion, some increase in birefringence above the additivity values in poly(DR1M-co-NBEM) would also be expected. This does not happen, hence it is very likely that dipolar interactions of the charge transfer type are the only driving force for the cooperative motion.

CONCLUSIONS

Two ester-type monomers with different polarity, BEM and NBEM, copolymerize with the azo-containing monomer DR1M in random fashion and form amorphous copolymers. The polarity of BEM is comparable to the polarity of DR1M, and the electronic spectra confirm that BEM and DR1M interact with each other more strongly than NBEM and DR1M do. A nonlinear increase of the photoinduced birefringence as a function of azo content is found in DR1M copolymers with the polar BEM group, while the increase is linear in copolymers with the nonpolar NBEM group. Comparison between the two copolymer series suggests that the dipolar association between BEM and DR1M is the major factor causing cooperative motion in these amorphous copolymers, enhancing the photoinduced birefringence.

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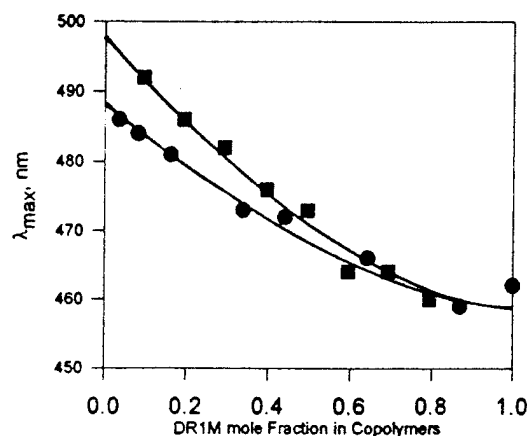


Fig. 1. Visible absorption maxima in electronic spectra of ■ poly(DR1M-co-BEM) and ● poly(DR1M-co-NBEM).

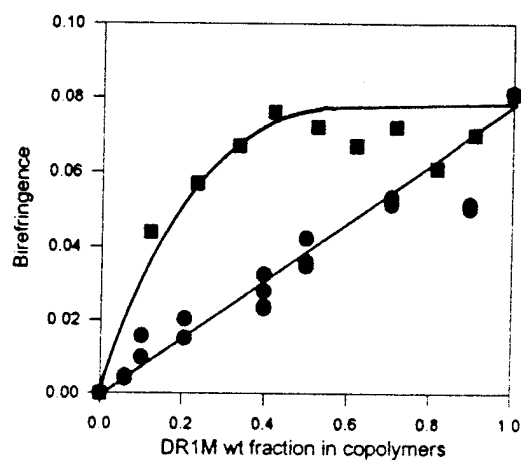


Fig. 2. Photoinduced birefringence of ■ poly(DR1M-co-BEM) and ● poly(DR1M-co-NBEM) vs. DR1M weight fraction